

PATENT SPECIFICATION

DRAWINGS ATTACHED

940,290

940,290



Date of Application and filing Complete Specification April 25, 1952.

No. 15687/62.

Application made in United States of America (No. 106,319) on April 28, 1961.

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ERRATA

SPECIFICATION No. 940,290

Page 2, line 60, after "by" delete "the"
Page 4, line 57, for "monoolfine" read
"mono-olefinic"

Page 4, line 63, for "atmosphere" read
"atmospheres"

Page 5, line 21, for "oration" read "oria-
tion"

Page 5, line 39, for "of" read "at"

Page 6, line 1 and 2, for "metres" read
"meters"

THE PATENT OFFICE

20th May 1964

- stage process for the production of high quality diesel fuel through the hydrotreating of highly aromatic, unsaturated hydrocarbon distillates boiling in excess of the gasoline boiling range and possessing the propensity to cause excessive deposition of coke and other carbonaceous material on the catalytic composite generally employed in such a process.
- 20 The present invention employs particular conditions of operation which inhibit the formation of coke and carbonaceous material, thereby permitting the catalytic composite to be employed for an extended period of time.
- 25 Hydrocarbon fractions frequently contain impurities which must be removed before they are considered suitable for their intended use, or which, when removed, enhance the value of the distillate for further processing.
- 30 These impurities include: sulfurous compounds, nitrogenous compounds, oxygenated compounds, and various metallic contaminants which cause the hydrocarbon distillates to exhibit corrosive tendencies and be foul-smelling, thereby making them less desirable for further use. In the case of a hydrocarbon charge stock intended for use as a diesel fuel, aromatic hydrocarbons are the "contaminants" which tend to lower the value of the diesel index.

Of the aforementioned impurities, combined sulfur is probably the most prevalent, existing in the hydrocarbon distillate, for example,

The same treatment is effective for the destructive removal of nitrogen-bearing molecules by converting them to the hydrocarbon counterparts and ammonia, the latter either being removed within a vapor phase, or adsorbed from the liquid product effluent. When existing in combined form, oxygen is less of a removal problem than either sulfur or nitrogen. Under the operating conditions employed in the hydrotreating process, oxygenated compounds are readily converted to the hydrocarbon counterpart and water, the latter being easily removed from the hydrocarbon product by any well-known means.

In addition to the aforementioned contaminants, the various hydrocarbon distillates, to which the present invention is applicable, contain an appreciable quantity of unsaturated hydrocarbons, both mono-olefinic and diolefinic, the latter including styrene, isoprene, dicyclopentadiene, and higher-boiling olefins. These unsaturated hydrocarbons are generally present in combination with aromatic hydrocarbons, and impart the coke-forming characteristics of the hydrocarbon distillate. When the distillate is subjected to hydrodesulfurization for the purpose of removing sulfur, nitrogen and oxygen, difficulty is frequently encountered in effecting the desired degree of reaction due to the formation of coke and other carbonaceous material. The deposition

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COMPLETE SPECIFICATION

Process for the Hydrorefining of Aromatic Hydrocarbon Distillates

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organised under the Laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a multiple-stage process for the production of high quality diesel fuel through the hydrorefining of highly aromatic, unsaturated hydrocarbon distillates boiling in excess of the gasoline boiling range and possessing the propensity to cause excessive deposition of coke and other carbonaceous material on the catalytic composite generally employed in such a process. The present invention employs particular conditions of operation which inhibit the formation of coke and carbonaceous material, thereby permitting the catalytic composite to be employed for an extended period of time.

Hydrocarbon fractions frequently contain impurities which must be removed before they are considered suitable for their intended use, or which, when removed, enhance the value of the distillate for further processing. These impurities include sulfurous compounds, nitrogenous compounds, oxygenated compounds, and various metallic contaminants which cause the hydrocarbon distillates to exhibit corrosive tendencies and be foul-smelling, thereby making them less desirable for further use. In the case of a hydrocarbon charge stock intended for use as a diesel fuel, aromatic hydrocarbons are the "contaminants" which tend to lower the value of the diesel index.

Of the aforementioned impurities, combined sulfur is probably the most prevalent, existing in the hydrocarbon distillate, for example,

as a mercaptan, thiophene or sulfide. Such sulfur is generally removed by the process of hydrodesulfurization, wherein the sulfur-bearing molecules are treated at an elevated temperature, generally in excess of 260° C. and often as high as 427° C. The reaction is effected in the presence of hydrogen and a suitable catalytic composite, whereby the sulfur-bearing molecules are converted to the corresponding hydrocarbon counterparts and hydrogen sulfide, the latter being removed from the process as a gaseous waste material. The same treatment is effective for the destructive removal of nitrogen-bearing molecules by converting them to the hydrocarbon counterparts and ammonia, the latter either being removed within a vapor phase, or adsorbed from the liquid product effluent. When existing in combined form, oxygen is less of a removal problem than either sulfur or nitrogen. Under the operating conditions employed in the hydrorefining process, oxygenated compounds are readily converted to the hydrocarbon counterpart and water, the latter being easily removed from the hydrocarbon product by any well-known means.

In addition to the aforementioned contaminants, the various hydrocarbon distillates, to which the present invention is applicable, contain an appreciable quantity of unsaturated hydrocarbons, both mono-olefinic and diolefinic, the latter including styrene, isoprene, dicyclopentadiene, and higher-boiling olefins. These unsaturated hydrocarbons are generally present in combination with aromatic hydrocarbons, and impart the coke-forming characteristics of the hydrocarbon distillate. When the distillate is subjected to hydrodesulfurization for the purpose of removing sulfur, nitrogen and oxygen, difficulty is frequently encountered in effecting the desired degree of reaction due to the formation of coke and other carbonaceous material. The deposition

		API Gravity × Aniline Point	
	of coke appears to result from the elevated temperatures, often in excess of 250° C., employed in the hydrodesulfurization process. The coke, which results from the thermal reaction of the unstable or coke-forming compounds within the distillate, generally appears as a deposit of solid, highly carbonaceous material on the catalytic composite, thereby shielding the catalytically active surfaces from the material being processed. These difficulties increase as the boiling range of the charge material increases, and are quite prevalent when the charge comprises hydrocarbons boiling in excess of the gasoline boiling range.	Diesel Index = $\frac{100}{\text{API Gravity} \times \text{Aniline Point}}$	65
5	Current processes for the hydrorefining of hydrocarbon mixtures are designed and operated for the purpose of removing the sulfurous and nitrogenous compounds, saturating the mono-olefinic and diolefinic hydrocarbons, while at the same time not substantially effecting the hydrogenation of the aromatic compounds. Such processes are adequate where the desired object is to produce aromatic-containing gasoline fractions, lubricants, and fuel oils. However, in many localities, the production of gasoline boiling range hydrocarbons containing large quantities of aromatic hydrocarbons is less important than the production of large quantities of high quality diesel fuel.	In comparing two hydrocarbon mixtures, in regard to utility as a diesel fuel, the lower the diesel index, the poorer the burning quality of the mixture. A low diesel index indicates a substantial concentration of aromatic hydrocarbons. In general, an acceptable diesel fuel possesses a diesel index in excess of 50.0, and preferably greater than 55.0. Hydrocarbon mixtures boiling in excess of the gasoline boiling range, such as coker distillates and heavy straight-run unsaturated middle-distillates indicate a diesel index of approximately 30. Such hydrocarbon distillates are not suitable for direct use as diesel fuels, and must necessarily be processed so as to increase the diesel index.	70
10	The object of the present invention is to provide a simple, effective method for hydrorefining hydrocarbon distillate fractions, and especially those boiling in excess of the gasoline boiling range, to produce high quality diesel fuel while avoiding the deposition of extremely large quantities of coke and other carbonaceous material on the hydrorefining catalytic composite.	The present invention relates to a process for the production of a high quality diesel fuel from an aromatic hydrocarbon distillate boiling in excess of the gasoline boiling range in which the distillate is reacted with hydrogen in a first reaction zone containing a hydrorefining catalyst, at least a portion of the effluent from the first reaction zone is introduced into a second reaction zone containing a hydrorefining catalyst and reacted therein with hydrogen. According to the present invention the quantity of catalyst disposed within the second reaction zone is at least 65.0% by volume of the total quantity of catalyst disposed within the first and second reaction zones and the portion of the effluent from the first reaction zone introduced into the second reaction zone is first cooled to a temperature such that the heat of reaction within the second reaction zone results in the effluent from the second reaction zone having a temperature of less than 427° C.	75
15	The quality of diesel fuel is determined by the rate at which the fuel burns; that is, the higher quality diesel fuels are those which have the faster rate of burning, with respect to diesel engines, a fast burning fuel is required because the fuel is injected into the engine cylinders in the liquid phase, rather than in the vapor phase as is customary with internal combustion engines employing gasoline boiling range hydrocarbons as fuel. Aromatic hydrocarbons have a much slower rate of burning than paraffinic hydrocarbons (including cycloparaffins), and the greater the concentration of aromatic hydrocarbons within the fuel, the less desirable the fuel for utilization in diesel engines. The quality of diesel fuels is frequently expressed in terms of the diesel index which may be calculated from the gravity of the fuel as expressed by the API (American Petroleum Institute) scale and the aniline point, the latter being determined by the ASTM Method D1012 and expressed in degrees Fahrenheit (ASTM Standards on Petroleum Products and Lubricants, published 1961 by American Society for Testing and Materials) using the formula	More particularly, in the process of the present invention, an aromatic hydrocarbon distillate boiling in excess of the gasoline boiling range is reacted with hydrogen at a temperature within the range of from 204° C. to 427° C. in a first reaction zone containing a hydro-refining catalyst, at least a portion of the resulting first reaction zone effluent is introduced into a second reaction zone containing a hydrorefining catalyst at an inter temperature such that the heat of reaction within the second zone results in the second reaction zone effluent having a temperature less than 427° C., the first reaction zone containing hydrorefining catalyst in an amount of from 5.0% to 35.0% by volume of the total quantity of catalyst disposed within the first and second reaction zones.	80
20		As stated above, when it is desired to produce a high-speed diesel fuel from an aromatic-containing, unsaturated hydrocarbon distillate by hydrorefining, the saturation of aromatics must be accomplished in addition	85
25			90
30			95
35			100
40			105
45			110
50			115
55			120
60			125

to the saturation of the mono-olefinic and diolefinic hydrocarbons as well as the reactions involved with the removal of sulfur and nitrogen. Of these reactions, the saturation of the olefinic hydrocarbons and the removal of the contaminating influences proceed at the faster rate, permitting therefor a higher liquid hourly space velocity. On the other hand, in order to effect the slower reaction involving saturation of aromatic hydrocarbons, a lower space velocity, or a greater quantity of catalyst for a like volume of liquid charge is necessary. Furthermore, the temperature of the charge material must be elevated to a level in excess of 204° C. in order to initiate the various desired reactions. Since the reactions are highly exothermic, there exists a significant heat of reaction which normally results in an exceedingly high temperature increase. In order to inhibit the excessive deposition of coke and carbonaceous material, there exists a maximum desirable operating temperature of 427° C. In single-stage hydro-refining of distillates boiling in excess of the gasoline boiling range the desired extent of reaction is not economically feasible due to the necessity of maintaining the temperature at a level less than the maximum. Multiple-stage processes have been proposed wherein the effluent from the first stage is passed into the second stage, the latter generally operating at greater severity (elevated temperature and pressure). These multiple-stage processes tend to decrease somewhat the formation of coke and carbonaceous material. Generally, these processes distribute the total quantity of catalyst utilized into as many equal proportions as reaction zones. Thus, in a two-stage process, the catalyst will be divided with 50% of the total quantity disposed within each zone.

However, these multiple-stage processes are primarily designed for the production of gasoline boiling range components or middle-distillate boiling range components, without requiring the saturation of aromatic hydrocarbons. Therefore, these processes do not suffice for the purpose of achieving the object of the present invention which is to produce a final product consisting essentially of naphthenes and paraffins, specifically having the object of saturating the aromatic hydrocarbons present in the fraction charged to the process.

When producing large volumetric yields of high quality diesel fuel (a fuel having a diesel index in excess of 50.0), it is preferred that the quantity of catalyst disposed within the first reaction zone lie within the range of from 5.0% to 15.0% by weight of the total quantity of catalyst.

By this method, the removal of contaminating sulfurous and nitrogenous compounds and the saturation of diolefinic and mono-olefinic hydrocarbons can be effected in the first reaction zone under the most advantageous conditions without excessive heat of reaction due

to the accompanying saturation of aromatic hydrocarbons. The saturation of the aromatic hydrocarbons is effected largely in the second reaction zone under the most advantageous conditions. The process of the present invention is thus effected in a sequence of contacting zones, each of which exists under conditions which are advantageously consistent with the chemical characteristics of the material passing therethrough.

The process of the present invention may be understood more clearly through reference to the accompanying drawing. In the interest of simplicity and clarity, various heaters, condensers, valves, controls, instruments, etc., have been eliminated from the drawing. Only those vessels and connecting lines necessary for the complete understanding of the process are indicated. The hydrocarbon charge stock used for illustration is a substantially unsaturated coker distillate, indicating a bromine number of 40.6 and a diesel index of 31.6, having a gravity, °API at 15.6° C, of 28.1 (specific gravity=0.887). In addition, the coker distillate is contaminated with 4.6% sulfur and 573 ppm. of nitrogen, and contains 49.0% aromatics. The charge stock enters the process through line 1 and is raised to the desired reaction zone inlet operating temperature within the range of 204° C. to 399° C. in heater 2. The heated charge is combined with an internally recycled, hydrogen-rich gaseous stream in line 21 and continues through line 3 into reactor 4. The product effluent from reactor 4, at a higher temperature than the inlet temperature due to the exothermic heat of reaction resulting from the saturation of mono-olefinic and diolefinic hydrocarbons and the removal of sulfurous and nitrogenous compounds, passes through line 5 into cooler 6. Cooler 6 is employed for the purpose of decreasing the temperature of the effluent from reactor 4 prior to passing this effluent through line 7 into the second-stage reactor 8. The means employed for lowering the temperature of the effluent from reactor 4, whether a cooler is illustrated, or various heat-exchangers or waste-heat boilers, is operated such that the temperature of the material entering reactor 8 is at a level whereby the heat of reaction within reactor 8 does not cause the temperature of the reactor 8 product effluent to exceed a level of 427° C. The reactor 8 effluent passes through line 9, cooler 10 and line 11 into separator 12. Separator 12 operates at essentially ambient temperature of about 54° C., and serves to separate the total product effluent from reactor 8 into gaseous and liquid phases. The gaseous phase containing hydrogen, ammonia, hydrogen sulfide, and light paraffinic hydrocarbons such as methane, ethane, and propane is withdrawn from separator 12 via line 17 by compressor 20 and is passed through line 21 into line 3

wherein it is admixed with the normally liquid charge to reactor 4. Make-up hydrogen, necessary to compensate for that consumed in the saturation of the mono-olefinic, diolefinic, and aromatic hydrocarbons, as well as in the removal of sulfurous and nitrogenous compounds, enters the process via line 22 on the suction side of compressor 20. At least a portion of the gaseous phase from separator 12 is removed via line 18 containing pressure control valve 19. This serves the purpose of preventing a build-up within the system of ammonia and hydrogen sulfide resulting from the conversion of the contaminating sulfurous and nitrogenous compounds. The liquid product effluent is passed from separator 12 via line 13 into stripper 14. Stripper 14 serves to remove additional ammonia, hydrogen sulfide and light paraffinic hydrocarbons from the system via line 15. Substantially completely saturated hydrocarbon products are withdrawn from the process via line 16.

Various modification of the illustrated flow may be made within the scope of the present process. For example separator 12 may be combined with additional separating and/or absorbing means. Water injection into line 9 may be provided for the purpose of absorbing the ammonia therein, the water and absorbed ammonia being removed via suitable liquid-level control means from separator 12. Similarly, the gaseous phase in line 17 may be treated so as to effect the substantially complete removal of hydrogen sulfide and/or light paraffinic hydrocarbons.

The fresh hydrocarbon charge is fed to reactor 4 in an amount which will result in a liquid hourly space velocity (defined as volumes of hydrocarbon charge per volume of catalyst disposed in the reaction zone) within the range of from 0.5 to 20.0. The space velocity through reactor 4 will be different from that through reactor 8 due to the varying quantities of catalyst disposed within the two reaction zones. The recycled, hydrogen-rich gas stream, indicated in the drawing as being admixed with the heated hydrocarbon distillate in line 3, will be supplied in an amount within the range of from 89 to 1038 liters per liter of hydrocarbon charge to reactor 4. Make-up hydrogen may be introduced into the process from any suitable exterior source to compensate for the hydrogen consumed within both stages of the process in the destructive removal of sulfurous and nitrogenous compounds, for the saturation of the diolefinic, monoolefinic and aromatic hydrocarbons, and to establish a suitable purity for recycle purposes.

The operating pressures in the reaction zones preferably will not differ greatly. These pressures will lie within the range of from 34 to 264 atmosphere, the pressure on the first stage being slightly higher than that on the second stage due to the pressure drop

normally experienced in passing the effluent from the former into the latter. Intermediate pressures within the range of 68 to 136 atmospheres are preferred. Both reaction zones will operate at an inlet temperature within the range of from 204° C. to 399° C. The inlet temperature is limited by the heat of reaction produced within the reaction zones. That is, the inlet temperature is so controlled that the heat of reaction produced will not cause the outlet temperature to exceed 427° C. Therefore, an essential feature of the present invention is that the effluent from the first reaction zone be subjected to cooling prior to entering the second reaction zone.

The multiple-stage hydrorefining process of the present invention is a catalytically conducted process, and the catalyst employed may be of the same chemical and physical composition in both of the reaction zones. Suitable hydrorefining catalytic composites comprise metallic components selected from Groups VI-A and VIII of the Periodic Table. Thus, the catalyst will comprise at least one metallic component selected from the group consisting of chromium, molybdenum, tungsten, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, and mixtures of two or more of these metals. The preferred catalytic composite for utilization in the multiple-stage process of the present invention comprises molybdenum and at least one metallic component selected from the iron-group of the Periodic Table including iron, cobalt and nickel. The molybdenum component will generally be in the greater concentration, from 4.0% to 30.0% by weight, while the iron-group metallic component will be present in an amount within the range of from 1.0% to 6.0% by weight, such concentrations being calculated on the basis of the elements. Suitable catalytic composites include the following: 5.7% by weight molybdenum, 2.2% by weight nickel and 0.25% by weight cobalt; 4.2% by weight nickel, 11.3% by weight molybdenum and 0.05% by weight cobalt; 17.0% by weight molybdenum and 1.5% by weight of nickel; 6.0% by weight nickel. The use of any particular catalytic composite is dependent, at least in part, upon the physical and/or chemical characteristics of the material to be processed. Generally, the catalytically active metallic components are composited with a suitable refractory inorganic oxide material including alumina, silica, zirconia, thorina, boria, titania, hafnia and mixtures of two or more of these oxides. Other components such as members of the halogen family, particularly fluorine and/or chlorine may be combined with the metallic components and the carrier material. In some instances, metallic components from Groups I and II of the Periodic Table may be combined with the composite to impart certain desired physical

and/or chemical characteristics. A particularly preferred carrier material comprises alumina and from 10% to 40% by weight of silica, based upon the total weight of the carrier material. The particular means employed for the manufacture of either the carrier material or the final catalytic composite is not considered to be essential to the present invention. Various suitable methods for such manufacture are known, and any such method may be used.

The process of the present invention is capable of successful efficient operation for an extended period of time. However, in virtually all catalytic processes there exists an inherent, naturally-occurring degree of deactivation of the catalytic composite employed. In the present two-stage hydrorefining process, the catalyst will gradually undergo deactivation as a result of the natural deterioration of the catalyst, the deposition of coke and other carbonaceous material during the prolonged period of operation, and the formation of various polymerization products, all of which have the tendency to shield the active centers and surfaces of the catalyst from the material being processed. The catalyst may be readily reactivated by a rather simple expediency which does not generally require an extended shutdown period. In those instances where the catalytic deactivation appears to have resulted from the deposition of coke and carbonaceous material, such material may be effectively removed by burning in an atmosphere of air. In many instances, a substantial quantity of the polymerization and copolymerization products may be removed by treating the catalyst with a circulating hydrogen-rich stream of elevated temperatures of from 260° C. to 593° C.

The following example is given to illustrate further the process of the present invention.

EXAMPLE

A catalyst consisting of an alumina-silica carrier material, composited with 0.05% by weight cobalt, 4.2% by weight nickel, 11.3% by weight molybdenum, calculated as the elements thereof, is disposed in two reaction zones arranged in series with 13.6% by volume of the total quantity of catalyst disposed in the first reaction zone. This catalyst is prepared by initially forming 1/16-inch spherical particles from a hydrosol comprising aluminum chloride, an acid solution of water glass and the necessary quantity of cobalt nitrate hexahydrate by the well-known oil-drop method as set forth in greater detail in U.S. Patent No. 2,620,314. After a high temperature calcination, the finished carrier material contains 88.0% by weight alumina and 12.0% by weight silica. The desired quantity of nickel and molybdenum are com-

bined with the carrier material through the utilization of impregnating techniques employing aqueous solutions of nickel nitrate hexahydrate and molybdic acid (85.0% by weight molybdic oxide). The impregnated composite is dried at a temperature of 93° C. and thereafter calcined at a temperature of 538° C. The calcined composite is preferably subsequently treated with a mixture of hydrogen and hydrogen sulfide to cause the metallic components to exist within the composite as the sulfides thereof.

TABLE I:

CHARGE STOCK PROPERTIES		
Gravity, °API at 15.6° C. -	-	28.1
Specific (15.6° C./15.6° C.) -	-	0.887
ASTM 100 ML Distillation, ° C.		
Initial Boiling Point -	-	214
5% -	-	222
10% -	-	229
30% -	-	252
50% -	-	276
70% -	-	303
90% -	-	335
95% -	-	347
End Point -	-	369
Aniline Point -	-	112.3
Diesel Index -	-	31.6
Sulfur, Wt % -	-	4.66
Nitrogen, PPM. -	-	573

The above distillate, which was a blend of coker distillate and a heavy straight run naphtha, after admixture with hydrogen in an amount of 534 liters/liter of charge, was passed, at a rate of 1312 cubic meters per day, into the first reaction zone at a temperature of about 316° C. and a pressure of 102 atmospheres. The total effluent from the first reaction zone, discharging therefrom at a temperature of about 399° C. was passed into a steam generator for the purpose of decreasing the temperature to a level of 329° C., prior to introducing the product effluent into the second reaction zone.

The temperature of the effluent from the second reaction zone was about 416° C. Said effluent was passed into a high pressure separator from which a hydrogen-rich gas stream was separated and recycled to combine with hydrocarbon distillate being charged to the first reaction zone. Make-up hydrogen, in an amount of about 1.5% by weight of the original hydrocarbon distillate charged, is admixed with the hydrogen-rich recycle gas introduced into the first reaction zone. The liquid hydrocarbon phase from the high pressure separating zone, containing hydrogen sulfide, ammonia and light paraffinic hydrocarbons including methane, ethane, and propane, was passed into a suitable stripping or fractionating zone from which approximately

5163 cubic metres per hour of dry gases are removed and 1,276 cubic metres per day of liquid product.

- 5 The normally liquid product effluent removed from the stripping means had the properties indicated in the following Table II:

TABLE II:	
PRODUCT PROPERTIES	
Gravity, °API at 15.6° C. - -	39.4
Specific (15.6° C./15.6° C.) -	0.828
ASTM 100 ML. Distillation, °C.	
Initial Boiling Point - - -	163
5% - - - - -	190
10% - - - - -	203
15 30% - - - - -	232
50% - - - - -	254
70% - - - - -	282
90% - - - - -	318
95% - - - - -	332
20 End Boiling Point - - - -	354
Aniline Point - - - - -	153.14
Diesel Index - - - - -	60.4
Sulfur, Wt. % - - - - -	0.05

- 25 It should be noted that 99.0% of the sulfur has been removed while the diesel index has been increased from 31.6 to a level of 60.4. Calculations have indicated that the yield of hexanes and heavier hydrocarbons, having the boiling range indicated in Table II, was within the range of 95.0% to 100% by volume, while the yield of dry gas was at the comparatively low level of 5.0% by weight of the total hydrocarbon distillate charged to the unit. It is significant that the quantity of dry gas includes 31.2 liters/liter of hydrogen sulfide resulting from the conversion of sulfurous compounds within the original hydrocarbon distillate.

- 40 One possessing skill within the art of petroleum processing will immediately recognize the utility of the material characterized by the properties given in Table II resulting from the present two-stage hydrotreating process as a highly suitable diesel fuel. This is indicated by the boiling range, and more particularly by the relatively high value of the diesel index and the comparatively low concentration of sulfur. Furthermore, the process consumes only about 1.5% by weight of hydrogen, based upon total liquid charge.

WHAT WE CLAIM IS:—

1. Process for the production of a high quality diesel fuel from an aromatic hydrocarbon distillate boiling in excess of the gasoline boiling range in which the distillate is reacted with hydrogen in a first reaction zone containing a hydrotreating catalyst, at least a portion of the effluent from the first reaction zone is introduced into a second reaction zone containing a hydro-refining catalyst and reacted therein with hydrogen, characterized in that the quantity of catalyst disposed within the second reaction zone is at least 65.0% by volume of the total quantity of catalyst disposed within the first and second reaction zones and the portion of the effluent from the first reaction zone to be introduced into the second reaction zone is first cooled to a temperature such that the heat of reaction within the second reaction zone results in the effluent from the second reaction zone having a temperature of less than 427° C.

2. Process according to claim 1 characterized in that the first reaction zone contains hydrotreating catalyst in an amount of from 5.0% to 35.0% by volume of the total quantity of catalyst disposed within the first and second reaction zones.

3. Process according to claim 1 characterized in that the distillate is reacted with hydrogen in the first reaction zone at a temperature within the range of from 204° C. to 427° C.

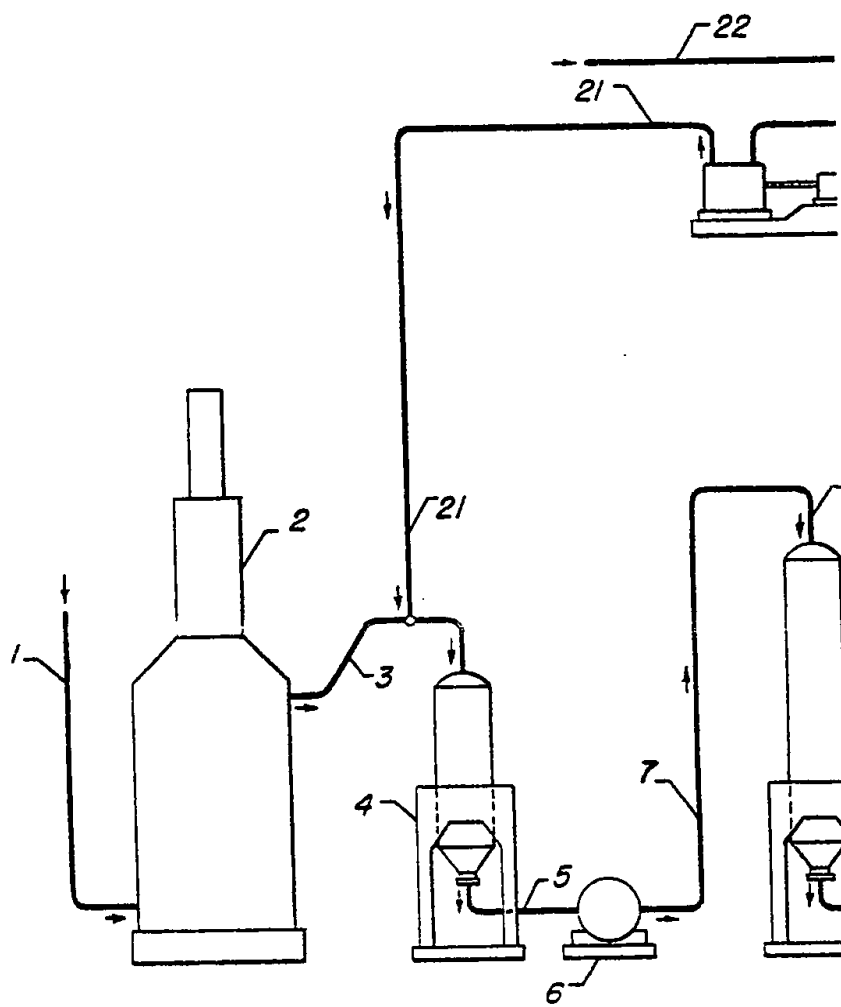
4. Process according to claim 1 characterized in that the hydrotreating catalyst in the first and second reaction zones is a catalytic composite having at least one metallic component selected from the metals of Groups VI-A and VIII of the Periodic Table.

5. Process according to claim 4 characterized in that the catalytic composite comprises molybdenum and at least one metallic component selected from the iron-group of the Periodic Table.

6. The process for the production of a high quality diesel fuel substantially as described.

7. The process for the production of a high quality diesel fuel substantially as described with reference to the drawing.

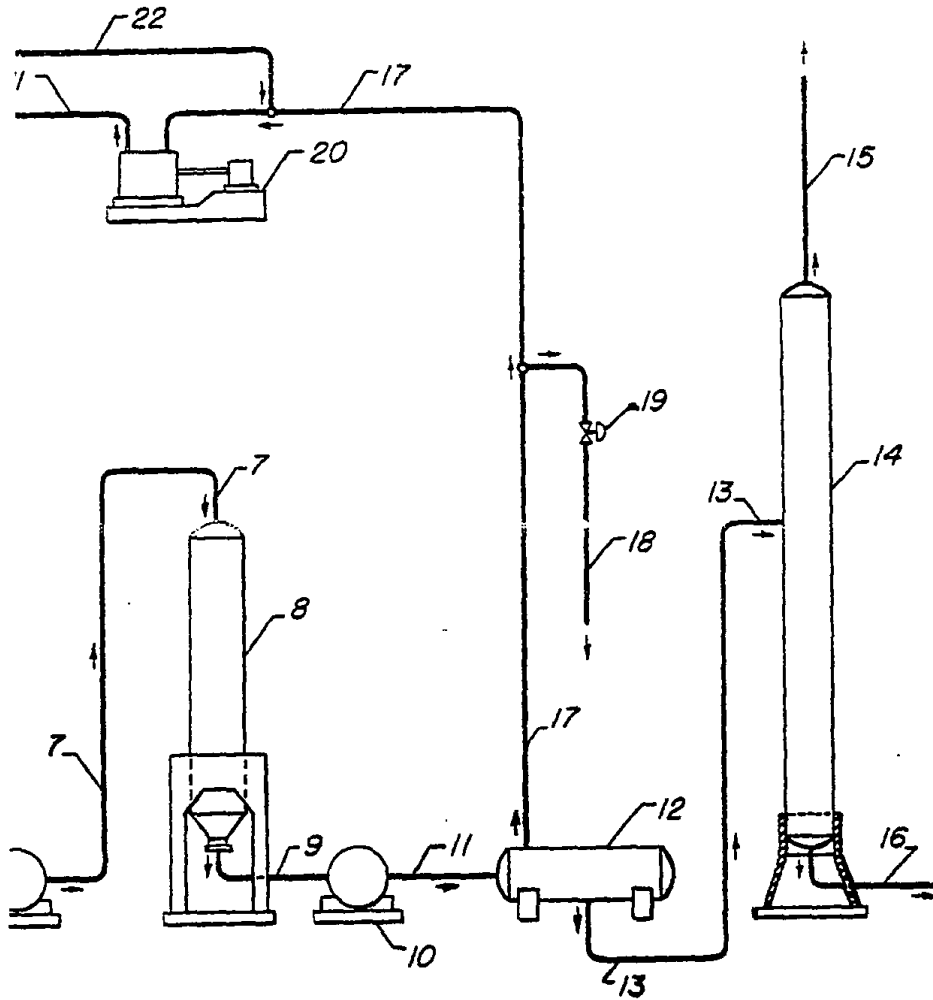
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940,290
1 SHEET

COMPLETE SPECIFICATION

This drawing is a reproduction of
the Original on a reduced scale.



The diagram illustrates a vacuum furnace system. A main chamber (1) is connected to a vacuum pump (2) via a valve (3). The chamber contains a sample (4) and a gas supply system. The gas supply system includes a gas cylinder (5) connected to a valve (6), which leads to a gas inlet (7) into the chamber. A gas outlet (8) is also shown. The chamber is equipped with a heating element (9) and a temperature sensor (10). The chamber is connected to a vacuum pump (11) via a valve (12). The vacuum pump is connected to a gas supply system (13) which includes a gas cylinder (14) and a valve (15). The gas supply system is connected to a gas inlet (16) into the chamber. The chamber is also connected to a gas outlet (17) which leads to a gas cylinder (18) and a valve (19). The gas supply system is connected to a gas inlet (20) into the chamber. The chamber is connected to a vacuum pump (21) via a valve (22).